Microwave-afterglow measurements of the dissociative recombination of molecular ions with electrons.

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Abstract

Microwave-afterglow measurements of the electron-temperature dependence of dissociative electron-ion recombination coefficients are subject to some recently discovered complications arising from non-uniformities of the microwave heating fields, inelastic collisions of electrons with molecular additives, and effects of vibrational excitation of ions and neutrals. This paper presents the results of recent experimental and theoretical work and examines consequences for earlier experimental data on electron-ion recombination. It appears that in some cases the electron temperatures attained by microwave-heating were actually lower than had been thought. As a consequence, the inferred dependences on electron temperature of the recombination coefficients were weaker than the true dependences.

I. Introduction

While much work, both theoretical [1-8] and experimental [4,9, 10,11], has been devoted to studies of electron-ion recombination during the past 40 years, we still possess only partial answers to partial questions. Recombination coefficients have been measured for many ionic species of interest, but often the dependence of the coefficients on electron energy or electron temperature is uncertain and we know little about effects of internal excitation, vibrational or electronic, of the recombining ions on the recombination process. There is almost complete lack of knowledge concerning the identity of the neutral products of dissociative recombination of polyatomic ions. This article reviews some of the more recent work on measurements of recombination coefficients using the microwave afterglow technique. The emphasis is on determinations of the dependence of the recombination coefficients on electron temperature and on related questions concerning vibrational excitation of the recombining ions. Recent work has revealed some previously unrecognized subtleties in the analysis of microwave afterglow plasmas which has forced us to reexamine some earlier results; some consequences of this reexamination will be discussed.

The process of interest here is dissociative recombination (DR) of molecular ions with electrons. Dissociative recombination, symbolically written as

$$e + AB^{+} \longrightarrow A^{*} + B^{*}, \qquad (1)$$

proceeds via the capture of the electron into a repulsive state of the product neutral, whose dissociation then irreversibly completes the recombination. As indicated by the asterisks, the neutral products may be formed with internal excitation, electronic and vibrational if A or B are molecular. The theory of DR originally was developed by Bates and Massey [1,2] and later extended by Bardsley [3,5]. The theory will not be discussed in detail here; the excellent review by Bardsley and Biondi [4] is referred to for a thorough discussion. Obviouly, precise calculation of recombination cross sections requires knowledge of the detailed energy states of molecules, which are not easily obtained by ab-initio calculations. It is customary to express the dependence of the recombination coefficient on electron temperature in the form of a power law

$$\alpha(T) = \alpha(300K)\ (T_e/300K)^{-x} \qquad (2)$$

where $\alpha(300K)$ is the recombination coefficient at 300K and the "temperature exponent" x is constant or nearly constant. Theory indicates that the value of x for simple diatomic ions should be on the order of 0.5 or slightly larger. Experimental measurements of recombination coefficients or cross sections have been carried out using two broad categories of techniques: The first makes use of

"swarm methods", i.e. one creates a gas plasma by a pulsed discharge, a burst of uv-light x-rays, and then determines the electron density loss during the afterglow phase of the plasma. The volume loss rate of electrons during the afterglow follows the differential equation

$$dn_e/dt = - \alpha\, n_e n_i \,, \qquad (3)$$

where n_e and n_i are the number densities of electrons and ions respectively and α denotes the recombination coefficient. When quasi-neutrality of the plasma can be assumed and negative ions are absent, the solution of Eq.3 can be written in the form

$$1/n_e(t) = 1/ n_e(t_o) + \alpha(t-t_o) \qquad (4)$$

which provides a convenient linear relationship for data fitting and the display of measured data. In actual experiments, loss of electrons by ambipolar diffusion to the walls usually is not negligible, so that numerical techniques have to employed to recover the recombination loss from the measured electron-density decay. The two basic forms of afterglow methods are the historically oldest "microwave-afterglow" technique developed by Biondi and coworkers [4] and the "flowing afterglow" technique, which is more commonly used for studies of ion-molecule reactions, but was more recently adapted by Smith and Adams [12,13] for electron-ion (also ion-ion) recombination measurements. Those authors use Langmuir probes to measure the electron densities and refer to their technique as "flowing afterglow/ Langmuir probe" (FALP).

In the second type of experiments, collisions between electrons and ions are studied in the low-pressure environment of either ion traps, as used by Dunn and coworkers [14], or merged-beam apparatus, a method developed by McGowan and colleagues [15]. The cross sections obtained by the latter techniques can be converted to rate coefficients by computing their maxwellian averages, provided that one has measured them over a sufficient range of energies (extrapolations to low energies may be necessary).

Compared to the beam methods, swarm techniques generally yield better absolute values of rate coefficients, a fact often implicitly acknowledged by proponents of the beam methods by their use of swarm data to normalize their data at a given energy. On the other hand, the higher energy resolution of the beam methods is a significant advantage and they do not suffer from the complicating phenomena often encountered in real laboratory plasmas.

The swarm methods are capable of covering a wide range of electron temperatures and a significantly smaller range of neutral temperatures. For instance, electron temperatures up to 5000K and higher can be attained easily by the use of selective microwave heating of electrons in afterglow plasmas, but, as will be seen later, the actual electron temperatures is often not as easy to determine as was once believed. The flowing-afterglow method (FALP)

[15,16] offers excellent flexibility in preparing plasmas of known ion composition, but the range of accessible temperatures is limited to that over which the neutral gas temperature can be varied (77 K to about 600K in practice). Higher gas temperatures (several 1000K) can be obtained in shock tubes. Cunningham and Hobson [16,17] applied this method to a number of recombination studies, but without using mass spectrometric identification of the plasma ions. The usefulness of shock heated plasmas for recombination studies is somewhat reduced by the lack knowledge concerning thermal equilibration of translational and vibrational degrees of freedom of the ions and neutrals in the plasma.

The interplay between laboratory studies of DR and data inferred from satellite observations of the earth's ionosphere has often been a strong motivating force. The great "laboratory in the sky" has some unique virtues, but the inference of recombination coefficients is so closely linked to many other collision processes, that in the absence of laboratory data one would not place much confidence in them. In some cases ionospheric observations, analyzed with the help of realistic ion-chemical models, have reproduced the laboratory results quite well.

In the following sections, we will briefly discuss the microwave afterglow method, state the assumptions made in the earlier forms of data analysis and then present some more recent results on specific ions. The critical remarks concerning earlier methods of data analysis should be seen in perspective. A large body of recombination data obtained by microwave afterglow methods is only marginally affected by the problems mentioned here.

II. The microwave afterglow technique.

The basic experimental method has been reviewed earlier in more detail by Biondi [4] who developed this technique. The remarks here are intended to give some background for the discussion of the more recent modifications in the analysis of such afterglows.

The basic principle of the microwave afterglow method is quite simple: Microwave breakdown is induced in a low-pressure gas (typically 10 to 40 Torr of a rare gas, contained in a microwave cavity) by application of a short (0.1 to 2 msec) pulse of microwave power (typically 50 W). The electron density after the pulse is then on the order of 1(9) to 1(10) cm^{-3}. Its decay during the afterglow phase, lasting typically 10 to 20 ms, is observed by measuring the frequency shift of a high-Q microwave cavity mode. If one decomposes the observed electron-density decay into that arising from recombination and that due to ambipolar diffusion of electrons to the cavity walls, one can accurately infer recombination rates for particular ion species, provided the following conditions are met:

One needs to be able to produce a plasma that contains the desired ion species but preferably no other ions in relevant

concentrations. Since the desired ions are not necessarily those of the buffer gas, one adds small amounts (1 to 1000 ppm) of other gases, usually molecular in character, and relies on Penning ionization, charge transfer, and ion-molecule reactions to produce the desired species. Some deliberate control over the final ion composition can be exercised by adjusting concentrations and sometimes gas temperatures. A mass spectrometer that analyzes the ion composition of the plasma is essential to this effort. The same mass spectrometer is also used to measure the decay of the relative (not absolute) ion densities during the afterglow and one demands that ion and electron densities "track" , i.e., that their decay curves have the same time dependence. Only when the experimental data show good "tracking" can one confidently assign an observed electron loss to recombination with a particular ion species.

In order to obtain accurate recombination data, diffusion losses of electrons should not mask the recombination losses, i.e., one wants a "recombination-controlled afterglow". The diffusion of electrons and ions is coupled by the space charge field (ambipolar diffusion) and it is described by an ambipolar diffusion coefficient D_a which depends on electron temperature in the form given by Schottky:

$$D_a = D_+(1 + T_e / T_+) \qquad (5)$$

Here, the subscripted quantities denote the ionic diffusion coefficient, and the electron and ion temperatures, respectively. The ion temperature is the same as the gas temperature in all cases of interest, but the electron temperature may be elevated by application of microwave power. The diffusion constants depend on the buffergas pressure and one chooses this pressure so that diffusion losses are not too rapid. For the commonly used rare gases, 10 to 40 Torr are sufficient.

The analysis of the electron density-decay due to combined effects of ambipolar diffusion and recombination, generally is carried out by fitting the observed decay to the results of a numerical model. If one increases the electron temperatures by application of continuous microwave power, diffusion losses increase (Eq.5) while recombination losses decrease. The result is that the inferred recombination rates become less accurate at high electron temperatures. In practice, this is not usually a serious problem for $T_e < 5000K$.

If the above conditions are met, the basic analysis of afterglow data is straightforward so long as the electrons and ions are in thermal equilibrium, i.e.,no microwave heating of electrons is employed. The subject of microwave heating of electrons will be discussed next.

Microwave heating of plasma electrons:

The microwave afterglow technique, in part, owes its attractiveness to the possibility of elevating the electron temperature to high values by application of microwave power to the experimental cavity. The physical mechanism by which the microwave field heats electrons is not fundamentally different from simple ohmic heating in an electric field: In the microwave field the electrons acquire an oscillatory energy, which is converted to random energy in collisions with neutral atoms. If the gas is atomic and excitation of the atoms by electron collisions need not be considered, the mean electron energy adjusts itself so that the power gained by this process equals that lost in "elastic" collisions. The power loss is then given by ν_c 2m/M, where m and M denote the masses of the electron and the neutral atoms and ν_c is the electron neutral collision frequency. It was shown by Margenau [18] that the electron energy distribution in this case is close to maxwellian.

The situation changes considerably, when the gas contains molecular admixtures, which in the experiment are required to produce the desired ions. Inelastic collisions, leading to vibrational and rotational excitation in those molecules, can lead to large fractional energy loss per collision with the result that the mean electron energy is reduced significantly below that attained in the pure atomic gas. That the effect is appreciable even when the molecular additives are present in only very small concentrations (10 to 1000 ppm), was pointed out by Phelps [19] and also by Penetrante and Bardsley [20]. It also became clear that the assumption of maxwellian energy distributions is not always justified when molecular additives are present. Only at high electron densities (near 1(10) cm-3) are electron-electron collisions effective in keeping the energy distributions close to maxwellian. These consequences of inelastic collisions with molecular additives were not always taken into account in some of the earlier work and some conclusions need to be reexamined.

A second complication, inadequately treated in earlier work, arises from the nonuniform microwave field distribution in the experimental cavity. The heating microwave (usually the TE_{111} mode) heats the electrons most effectively where the field is large. The question arises then whether or nor heat conduction within the electron gas can be counted on to make the electron temperature uniform over the volume of interest. A simple criterion may be used to assess the efficiency of heat transfer: We are asking how many collisions an electron has to make with the gas atoms in order to reach its equilibrium mean energy appropiate to the local field. The number is on the order of n= M/2m in an atomic gas of mass M. While equilibrating its energy the electron diffuses a distance of $\delta(2n)^{1/2}$, where δ is the electron mean free path for momentum transfer. Thus, when the distance $L=\delta\ (M/m)^{1/2}$ is small compared to a typical length scale (e.g. the cavity radius R) the

electron gas will have a highly non-uniform temperature distribution; in the opposite case, L>>R, the temperature should be fairly uniform, even though the microwave field is not. The estimate needs to be modified when molecular additives are present.

It turns out that under the conditions of many such experiments the length L is on the same order as the cavity radius, i.e. neither limiting case is approached, but the temperature distribution clearly is not uniform. In earlier work the experimentalists generally assumed a spatially uniform temperature and believed that their measured recombination rate coefficients referred to an isothermal plasma whose temperature could be calculated from the microwave power entering the cavity and other known quantities. However, a detailed numerical analysis of the heat transfer problem by Dulaney et al. [21] showed that T_e may actually vary spatially by factors of three and more for typical conditions of pressures and cavity sizes. This finding greatly complicates the analysis of the data: Neither the recombination coefficient nor the the rate of ambipolar diffusion are spatially uniform and the numerical models used to analyze the data become rather complex. The non-uniformities of the electron temperature become even more pronounced when inelastic collisions of electrons with molecules have to be included.

Dulaney et al. [21] have constructed a numerical model and have applied this model to the analysis of several afterglow measurements of recombination coefficients. Details are described in a separate publication [21]. Their model takes into account effects of inelastic collisions of electrons with neutral molecules and it treats power balance, heat transfer, recombination and ambipolar diffusion locally, rather than by using quantities averaged over the plasma volume. The predictions of the model calculation are then compared to a simplified analysis of the data in order to find the recombination coefficients which best fit the observed data. The full numerical treatment so far has been applied to several measurements of recombination coefficients. In several cases, to be discused later, the results differed significantly from those obtained using the earlier, simpler analysis. Some conclusions of other earlier measurements may be affected by the new findings, but at present one can only estimate the severity of the corrections. This will be done in the following sections on particular ions.

II. Measurements for particular ion species

Recombination of diatomic rare-gas ions

The measurements of electron-ion recombination of diatomic rare gas ions by Biondi and coworkers [22-25] were carried out in pure rare gases so that the problem of inelastic collisions with molecular constituents in the plasma does not arise. The second problem, non-uniformities in T_e arising from non-uniform microwave heating fields, by itself is not very serious and, furthermore, those

measurements were carried out in plasma containers comprising only a small part of the microwave cavity or waveguide. Thus the effect of nonuniform heating fields should have been less important. While no quantitative reanalyses of those early measurements have been performed, it seems unlikely that the inferred temperature dependences of the recombination were significantly in error.
A compilation of data pertaining to diatomic rare-gas is given in Table I.

Recombination of NO^+ ions

The recombination of NO^+ with electrons is of particular interest as an important electron removal process in the F-region of the earth's ionosphere. The electron temperatures of greatest interest are on the order of 2000 K, higher than can be attained in the laboratory by heating the experimental apparatus. Thus, the microwave heating of electrons provided an important means of measuring recombination rates in that temperature range.

Earlier microwave afterglow work by Huang et al [26] extended the room temperature measurements by Weller et al. [27] to temperatures then believed to be near 5000 K. The recombination rates were then thought to fall off with temperature as $T_e^{-0.37}$.

The results seemed somewhat surprising since the trapped-ion measurements by Walls and Dunn [14] had yielded cross sections implying a considerably stronger temperature dependence (as $T_e^{-0.85}$). The stronger temperature dependence also seemed to be in better agreement with that inferred from ionospheric modeling and observational data [28]. The ensuing debate initially focussed on possible vibrational excitation of the NO^+ ions in the afterglow measurements, but evidence in support of such effects was not found and there appeared to be no good reason to assume that, even if they were present, vibrationally excited ions would behave differently from those in the lowest vibrational state.

The microwave afterglow measurements of Huang et al [26] were subsequently repeated by Dulaney et al [21] using essentially the same experimental method. It had been pointed out by then [19,20] that the analysis of microwave heating of electrons had to be modified by including a term taking into account energy loss due to inelastic collisions with the neutral nitric oxide molecules. Calculations by Penetrante and Bardsley [20] on this problem showed that the "inelastic cooling" was not negligible and that furthermore the velocity distributions of the electrons would be close to maxwellian only at high electron densities. Dulaney et al [21] examined the consequences of this finding for their experiment and found that the problem was in addition complicated by spatial nonuniformities of the electron temperature arising from the nonuniform microwave field distribution. Using the more accurate model of the microwave-heated plasma, described earlier, they obtained results in agreement with the trapped-ion data.

The results of different measurements are listed in Table II. A comparison of data shows that there is now quite good agreement between all measurements and the data inferred from ionospheric observations. The earlier results by Huang et al. were clearly in error.

Recombination of N_2^+ ions:

N_2^+ ions are common in many laboratory discharges and also in the earth's ionosphere. The first measurements of the variation of $\alpha(N_2^+)$ with electron temperature were carried out by Mehr and Biondi [21] whose results may be expressed in the form:

$$\alpha(N_2^+) = (1.8 \pm 0.4)\ x(T/300)^{-0.39} \times 10^{-7}\ \ cm^3/s \qquad (6)$$

Recombination coefficients inferred from ionospheric modeling and observational data by Orsini et al. [30] generally have been higher than the laboratory data, and it was suggested that the higher ionospheric coefficients referred to vibrationally excited ions. In view of the complexity of the ionospheric processes affecting N_2^+ the evidence in support of this suggestion, however, must be regarded as weak and Biondi [31] pointed out that a strong enhancement of $\alpha(N_2^+)$ by vibrational excitation is very unlikely.

The effect of vibrational temperatures of ions on their recombination rates nevertheless was and still is of great interest. An experiment intended to address this question of was performed by Zipf [32], who used a microwave afterglow technique and monitored the decay of recombining N_2^+ ions in the v=0,1,2 states by laser induced fluorescence. His experiments were carried out in neon buffer gas (6.0 Torr) with a small (0.3 mTorr) addition of nitrogen. The decay rates of N_2^+ ions in all three observed vibrational states were seen to be nearly identical. From this observation Zipf inferred recombination rates of 2.15 $x10^{-7}$ cm^3/s for v=0 ions, 13% and 26 % larger values for v=1 and v=2 ions, respectively.

Zipf's interpretation that he had measured recombination coefficients for ions in particular vibrational states and that these were nearly independent of vibrational state seemed convincing at that time, but it is probably not justified for the following reason: It was found later [33] that vibrationally excited N_2^+ ions are quenched quite rapidly by neutral, vibrationally unexcited nitrogen in symmetric charge transfer collisions, i.e. there is a strong coupling between the vibrational states of ions and neutrals. Under the conditions of Zipf's experiment, exchange of vibrational energy between neutrals and ions would take place on a time scale of tens of μsec, short compared to the afterglow decay time of many msec. Zipf's finding of persistent vibrational excitation of the ions

most likely indicates that the neutral nitrogen was vibrationally excited in the microwave discharge and during the afterglow remained at a temperature near 1500 K, the same as the ion temperature inferred by Zipf. The observed recombination then most likely refers to a strongly coupled system of ions in thermal equilibrium with the neutral nitrogen, not to ions in particular vibrational states. In conclusion: Even though Zipf may not have succeeded in measuring recombination rates for ions in specified vibrational states, his results show that the effective recombination rate for an ion population with a vibrational temperature near 1500 K is quite similar to that of ground-state ions.

Measurements of the recombination coefficient of nitrogen ions have also been carried out by Cunningham and Hobson [17], using a shock tube technique. In their experiment both neutral and electron temperatures were elevated, but their results agreed well with those of Mehr and Biondi [29] obtained by heating of the electrons only. These authors believed that their ions were in the vibrational ground state. Merged-beam experiments by Mul and McGowan [15] yielded recombination coefficients about 30 % higher than those of Mehr and Biondi with a somewhat stronger temperature dependence. The measured recombination coefficients are tabulated in Table III.

The presence of vibrationally hot molecules in afterglow plasmas found by Zipf [32] is also of interest for a different reason: One might expect that the electron and vibrational temperatures in an afterglow lasma would tend to equilibrate, the energy exchange mechanism being inelastic or supereleastic collisions between electrons and neutral molecules. As a consequence, a "room temperature" afterglow plasma might actually contain electrons at a high temperature and the observed electron ions recombination rates would be erroneously low. Hurle [34] discussed the importance of such effects in pure nitrogen plasmas. However, using the cross sections given by Hurle one estimates that in afterglow plasmas containing only small (~100ppm) concentrations of nitrogen in a large amount of buffergas this effect should be negligible and consequently the effect on determinations of recombination rates should also be unimportant.

The electron temperatures calculated by Mehr and Biondi [29] are still expected to be essentially correct. Also, while the assumption of spatially uniform electron temperatures made by those authors may not have been justified, the errors should be within the stated uncertainties.

Recombination of O_2^+ ions:

Recombination coefficients for O_2^+ ions have been measured by Mehr and Biondi [29] in a microwave afterglow experiment, by Cunningham and Hobson [17] in a shock tube, by Walls and Dunn [14] in a trapped ion experiment, by Mul and McGowan [15] in a merged-beam apparatus, and by Alge et al. [13] using the FALP method. The results

(see Table IV) are in remarkably good agreement both as to the absolute magnitude and the dependence on electron energy or temperature.

Since the dependence on electron temperature in this case seemed well established, it was of interest to see if application of the more sophisticated methods of afterglow analysis developed by Dulaney et al [21] to the data by Mehr and Biondi [29] would reproduce the same dependence on electron temperature. Numerical calculations have been carried out which included the effects of inelastic collisions of electrons and spatial nonuniformities in the electron temperature. The results indicated that even at the highest electron temperatures used in the experiment the necessary corrections to the recombination coefficients would be only on the order of 5%. The measurements by Mehr and Biondi, however, should be interpreted as referring to a non-isothermal plasma. The electron temperatures given by them are to be understood as averages over the plasma volume.

Recombination of cluster ions:

In many low-temperature plasmas, especially those containing polar molecules such as water or ammonia, ion chemical reactions rapidly form complex cluster ions. Good examples are protons clustered to several (1 to 5) water or ammonia molecules. It has ben known for some time [35,36,37] that these ions recombine very efficiently with electrons and thus may be the agent controlling electron densities in the D-region of the ionosphere and many laboratory plasmas. The large magnitude of the recombination coefficients of such ions is not as surprising as the observed lack of dependence on electron temperature (see Table V for data).

There are few experimental data on the energy dependence of cluster-ion recombination, all of which were obtained by microwave afterglow methods [35-37]. The lack of a temperature dependence of the observed recombination coefficients is difficult to understand from the point of view of theory. Two interpretations seem possible: If the experimental data are accepted as true, the mechanism of the recombination of cluster ions with electrons must be fundamentally different from that for simple, diatomic ions. Alternatively, one might ask whether the electron temperature was actually increased in the experiments. The inelastic energy loss of electrons in the presence of polar gases is unusually large and high concentrations of such gases were required to produce the cluster ions by three-body ion-molecule association. A clear answer can not be given at the present time, since the relevant calculations have not been carried out and often reliable energy loss cross sections with polar gases are not available. There is, however, a strong suspicion that the apparent lack of temperature dependence of the recombination of cluster ions was caused by absence of significant heating of the electrons. It seems possible that the true temperature dependence of

these recombination coefficients is as strong as that for other ions, but that the experiments failed to observe it.

Recombination of dimer and trimer ions: O_4^+, N_4^+, CO^+CO, $CO^+(CO)_n$

Recombination of these ions with electrons has been investigated by Whitaker et al. [38,39] and Dulaney et al. [40] using the microwave-afterglow method and microwave heating of electrons (see Table VI). The concentrations of the molecular gases in the plasma generally have to be larger than those in studies of the monomer ions. Dulaney et al. [40] analyzed their O_4^+ data taking into account effects of inelasic collisions of electrons with oxygen molecules and found that those effects were clearly important. This was demonstrated experimentally by measuring recombination rates for different oxygen concentrations. It was observed that an increase in the oxygen concentration tended to increase the observed electron loss rate. This is exactly what one expects, since the effect of oxygen is to decrease the electron temperature and hence to increase the recombination rate.

The final results of Dulaney's et al. measurements and analysis may be written in the form:

$$\alpha(O_4^+)=(4.2\pm0.4)\times10^{-6}\ (T_e/300)^{-0.48}\ cm^3/s \qquad (7)$$

It appears that the earlier measurements of N_4^+ and CO^+CO recombination by Whitaker et al. [38,39] should be revised slightly to correct for the reduction of the electron temperature due to inelastic collisions of electrons with nitrogen or carbon monoxide molecules. Estimates suggest that the true temperature exponent may be closer to 0.5, i.e., the same as for simple diatomic ions.

Recombination of H_3^+ ions:

The recombination of H_3^+ ions with electrons is an important electron removal process in many laboratory plasmas, in planetary atmospheres and in interstellar clouds. In hydrogen plasmas, the ion is usually formed by the ion-molecule reaction

$$H_2^+ + H_2 \longrightarrow H_3^+ + H$$

which leaves the product ion with several quanta of vibrational energy. Conversion of H_3^+ ions to H_5^+ by three-body association occurs, but at low pressures the equilibrium is on the side of the H_3^+ ion.

Measurements of the recombination coefficients of mass identified H_3^+ ions with electrons were first carried out by Leu et al. [41] using the microwave afterglow method. The dependence of the recombination coefficient on electron temperture was the subject of later work by Macdonald et al. [42]. The results indicated a fairly "normal" recombination coefficients of 2 to 3 x 10^{-7} cm^3/s

at 300 K, falling of with temperature above 400 K as $T^{-0.88}$. From cross section measurements in a merged-beam experiment, Mitchell et al. [43] inferred similar absolute values for the recombination coefficient, but they observed a somewhat weaker variation with electron energy (see Table VII for measured data).

The situation changed drastically as a result of theoretical calculations by Michels and Hobbs [44] and by subsequent experimental work of Adams et al. and Smith and Adams [13,46] who used the flowing afterglow/Langmuir probe (FALP) method developed by them. Michels and Hobbs' theoretical work showed that due to lack of suitable potential -curve crossings recombination of H_3^+ ions in low vibrational states should be far slower than the earlier experiments indicated. Subsequently, the experiments by Adams et al.[44] yielded coefficients less than one tenth of the earlier results, supporting Michels' prediction. The question then arose, why both the merged-beam and the afterglow measurements had indicated much higher values. Vibrational excitation of the H_3^+ ions be invoked to explain the merged beam data: In the usual low-pressure ion sources employed with beam experiments, vibrationally excited H_3^+ ions are expected to be produced and they are not likely to be quenched in collisions. Subsequent merged-beam measurements, employing ion sources designed to promote quenching [46], resulted in substantially lower recombination cross sections [47] (these results are still considered to be preliminary by the investigators).

In the microwave afterglow experiments, just as in the FALP experiment, quenching collisions with neutral H_2 should have been effective, so that vibrational excitation cannot be invoked. Some additional work was performed to find other possible causes for this discrepancy. The presently most plausible explanation is that the microwave afterglow measurements were contaminated by an impurity ion in the plasma: A persistent impurity ion having a mass of 17 amu was observed with an abundance of 10% or less of that of H_3^+. The ion was then expected to be NH_3^+, and its effect on the recombination measurements was deemed to be negligible. Later work in similar gas mixtures also showed the presence of a 17 amu impurity ion: by isotopic substitution (using deuterium instead of hydrogen), the 17 amu ion was identified as CH_5^+, an ion with a large electron ion recombination coefficient ($\alpha = 1.1 \times 10^{-6}$ cm^3/sec [46]). It appears likely that a significant fraction of the observed recombination loss, originally ascribed to H_3^+, was largely due to this impurity ion. In view of this problem, the determinations of $\alpha(H_3^+)$ by Leu et al. [41] and the measurements of its dependence on T_e by Macdonald et al. [42] must be regarded as questionable and a discussion of possible effects of inelastic electron collisions on the quoted electron temperatures is not meaningful at the present time.

Recombination of HCO^+ ions

HCO^+ is an important ion in the interstellar medium, in combustion flames, and possibly in some planetary ionospheres. Measurements of its reombination coefficient at low temperatures have been carried out by Leu et al. [48] (at 205K and 300 K) in a microwave afterglow experiment and by Adams et al. [46] (at 95K and 300K) in a flowing afterglow/Langmuir probe (FALP) apparatus.

Ganguli et al. [49] employed the microwave afterglow technique including microwave heating to cover the electron temperature range from 293 K to 5500 K. Their data analysis included effects of spatial nonuniformities in the electron temperature and inelastic collisions of electrons with hydrogen and carbon monoxide, the two gases used to generate the HCO^+ ions. Their results can be written in the form:

$$\alpha(HCO^+) = (2.4\pm0.4)\times10^{-7}(T_e/300)^{-0.69}\ cm^3/s$$

Unfortunately, the recombination coefficient at 300 K is larger by about a factor of two than that observed by Adams et al.[45] in the FALP experiment. Since the data analysis by Ganguli et al. [50] specifically included a correction for impurity ions (H_3O^+ was present in the experiment in minor concentrations) the cause of the discrepancy may lie elsewhere.

IV Summary and conclusions

It is clear that the inference of electron-ion recombination coefficient from microwave afterglow data is sometimes more complicated than had been thought, but this should be seen in the proper perspective. Most of the data produced by this experimental technique reamain valid, others may slightly underestimate the dependence of the recombination coefficients on electron temperature. The complications can often be taken into account by improved data analysis. The recombination data pertaining to polar-molecule cluster ions must be regarded with suspicion since the observed lack of dependence on electron temperature may be an experimental artifact.

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Table I. Measured recombination coefficients for rare-gas ions

Ion	α(300K)[cm^3/s] x	Temp.[K]	method	Reference
Ne_2^+	1.75±0.2 [-7] 0.49	300-4600	μwa-ms	22
Ar_2^+	9.1±1.0 [-7] 0.61	300-8500	μwa	23
Kr_2^+	1.6±0.2 [-6] 0.55	300-8400	μwa	24
Xe_2^+	2.3±0.2 [-6] 0.6	300-7500	μwa	25

(see Table II for explanation of abbreviations)

Table II. Measured recombination coefficients for NO^+ ions

Ion	α(300K)[cm^3/s]	x	Temp. [K]	method	remarks	Reference
NO^+	4.3±0.3 [-7]	0.38	380-5470	μwa-ms	(A)	26
NO^+	4.2 [-7]	0.9	200-600	FALP		12
NO^+	2.3 [-7]	0.5	>10,000	MB		15
NO^+	4.3 [-7]	0.85	5000	trap		14
NO^+	4.4 [-7]	0.75	300-4500	μwa-ms	(B)	21

Abbreviations: μwa-ms: microwave afterglow-mass spectrometer
μwa : microwave afterglow
MB : merged beam
FALP : flowing afterglow/Langmuir probe
shock : shock tube
trap : ion trap

Remarks: (A) Data analysis did not allow for inelastic collisions of electrons with NO and temperature non-uniformities.
(B) Data analysis included effects of inelastic of inelastic collisions and temperature non-uniformities

Table III. Measured recombination coefficients for N_2^+ ions.

Ion	α(300K)[cm^3/s]	x	Temp.[K]	method	remarks	Reference
N_2^+	1.8±0.4 [-7]	0.39	300-5000	μwa-ms		29
N_2^+	3.5 [-7]	0.5	300- >10000	MB		15
N_2^+	2.2 [-7]	--	300	μwa-ms	(A)	32
N_2^+	1.78[-7]	0.37	700-2700	shock-tube	(B)	17

(see Table II for explanation of abbreviations)

Remarks: (A) see text for discussion of vibrational excitation in that experiment. (B) the gas temperature was varied, but vibrational state of the ion was believed to be the ground state.

Table IV. Measured recombination coefficients for O_2^+ ions.

Ion	α(300K)[cm^3/s]	x	Temp. [K]	method	Reference
O_2^+	1.95±0.2 [-7]	0.7 0.56	300-1200 1200-5000	μwa-ms	29
O_2^+	1.95 [-7]	0.7	200-600	FALP	12
O_2^+	1.95 [-7]	0.66	200-5000	trap	14
O_2^+	2.3 [-7]	0.5	300-10000	MB	15

(see Table II for explanation of abbreviations)

Table V. Measured recombination coefficients for cluster ions

Ion	α(300K)[cm/s]	x	Temp.[K]	method	remarks	Reference
$H_3O^+(H_2O)$	2.5±0.5 [-6]	0.08	300-8000	μwa-ms	(A)	35
$H_3O^+(H_2O)_2$	3.0±0.6 [-6]	0.08	300-8000	μwa-ms	(A)	35
$H_3O^+(H_2O)_3$	3.6±0.7 [-6]	0	300-8000	μwa-ms	(A)	35
$H_3O^+(H_2O)_4$	~5 [-6]	0	300-8000	μwa-ms	(A)	35
$H_3O^+(H_2O)_5$	~5 [-6]	0	300-8000	μwa-ms	(A)	35
$NH_4^+(NH_3)$	2.82 [-6]	0.147	300-3000	μwa-ms	(A)	36
$NH_4^+(NH_3)_2$	2.68 [-6]	0.05	300-3000	μwa-ms	(A)	36
$NH_4^+(NH_3)_3$	~3 [-6]	0	200	μwa-ms	(A)	36
$NH_4^+(NH_3)_4$	~3 [-6]	0	200	μwa-ms	(A)	36

(see Table II for explanation of abbreviations)

Remarks: (A) The observed small values of x may due to failure of attaining the stated electron temperatures in the experiments.

Table VI. Measured recombination coefficients for dimer and trimer ions

Ion	α(300K)[cm^3/s]	x	Temp.[K]	method	remarks	Reference
$N_2^+ N_2$	1.4±0.2 [-6]	0.41	300-6000	μwm-ms	(A)	38
$CO^+ CO$	1.3±0.3 [-6]	0.34	300-4000	μwm-ms	(A)	38
$CO^+ (CO)_2$	1.9±0.4 [-6]	~0	300-1000	μwm-ms	(A)	38
		0.33	1000-9000	μwm-ms	(A)	38
$O_2^+ O_2$	4.2±0.4 [-6]	0.48	143-5500	μwm-ms	(B)	40

(see Table II for explanation of abbreviations)

Remarks: (A) The true values of x are likely to be closer to 0.5
(B) Data analysed using the improved method.

Table VII. Measured recombination coefficients for H_3^+ ions.

Ion	α(300K)[cm/s] x	Temp.[K]	method	remarks	Reference
H_3^+	2.3 [-7]	300	μwa-ms	(A)	41
H_3^+	1.7 [-7] 1.0	500-3000	μwa-ms	(A)	42
H_3^+	~3.5[-7] ~0.5	(0.01-0.7 eV)	MB	(B)	43
H_3^+	<2 [-8] ---	95K, 300K	FALP	(C)	13

(see Table II for explanation of abbreviations)

Remarks: (A) The measured recombination coefficients may have been affected by impurity ions in the afterglow.
(B) The ions were most likely vibrationally excited.
(C) The ions were most likely in the vibrational ground state.

Table VIII. Measured recombination coefficients for HCO^+ ions

Ion	α(300K)[cm^3/s]	x	Temp. [K]	method	Reference
HCO^+	2.0[-7]	~1	300, 205	μwa-ms	48
HCO^+	1.1[-7]	~0.8	300, 95	FALP	13
HCO^+	2.4±0.4 [-7]	0.69	293-5500	μwa-ms	49

(see Table II for explanation of abbreviations)